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Thermophysical Properties of Solid Phase Zirconium at High Temperatures[1]

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This paper presents experimental results on the thermophysical properties of relatively pure polycrystalline zirconium samples in the solid phase from room temperature up to near the melting point. The specific heat capacity and specific electrical resistivity were measured from 290 to 1970 K, the hemispherical total emissivity from 1400 to 2000 K, the normal spectral emissivity from 1480 to 1940 K, and the thermal diffusivity in the range from 290 to 1470 K. From these data, the thermal conductivity and Lorentz number were computed in the range from 290 to 1470 K. For necessary corrections the most recent values of the linear thermal expansion from the literature have been used. Subsecond pulse calorimetry for measuring heat capacity, specific electrical resistivity, and both emissivities and the laser flash method for measuring thermal diffusivity were applied. Samples in the form of a thin rod and in the form of a thin disk were used in the first and second methods, respectively. Measurement uncertainties were generally about 3% for heat capacity, 1.6% for specific electrical resistivity, 3–10% for the two emissivities, and from less than 1% up to 6% for thermal diffusivity. All the results are discussed in reference to available literature data.

KEY WORDS: electrical resistivity; hemispherical total emissivity; high temperatures; laser flash method; normal spectral emissivity; specific heat capacity; subsecond pulse calorimetry; thermal diffusivity; zirconium

1. INTRODUCTION

Due to its role in many industrial applications, especially in nuclear power engineering, and because of several remarkable features, such as the presence of intrinsic phonon anomalies at high temperatures, the thermophysical

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properties of zirconium have been the subject of numerous experimental and theoretical research. The position of the structural hcp/bcc phase transition at the approximate mid-point between room temperature and its melting point makes the temperature regions of both solid phases relatively wide and easily accessible for various experimental thermophysical property studies. Moreover, having discontinuities in most thermophysical properties near the phase transition temperature, zirconium represents a good reference material both for method evaluation and for the comparison of different experimental techniques.

Starting from Zwicker [1], who first pointed out the temperature region of the phase transition, thermophysical data of zirconium have been studied and published by many authors over eight decades. Probably the most comprehensive and fairly recent thermophysical investigation of this metal was given in 1987 by Guillermet [2]. His thermophysical data have been estimated on the basis of a theoretical model with the use of previously published experimental information.

Regardless of the great number of available experimental and theoretical data on zirconium, there were several reasons for undertaking this work. First, as Guillermet stated in [2], there was still a deficiency of information on the thermophysical properties of zirconium at high temperatures, especially in the region of its bcc phase. Although several papers about zirconium properties in that region have been published since then [3–7] this work could also be a contribution in that sense. Second, there are few available literature data on the thermal diffusivity of zirconium, especially in its bcc phase. In fact, authors of this paper found in that region only data published by Zinovyev [8] and estimated values given by Touloukian et al. [9]. Besides, due to difficulties in measuring the thermal conductivity at very high temperatures, there are only a few authors who published such data. In this work, however, by measuring the thermal diffusivity of both hcp and bcc phases and by using heat capacity information obtained from the sample from the same batch, the estimation of the thermal conductivity over a wide temperature range became also possible. In addition, as zirconium tends to form strong bonds with oxygen at high temperatures and changes its chemical composition, prolonged experiments under such conditions makes the measurement results less reliable, particularly those of surface properties. For measuring the hemispherical total and normal spectral emissivities, this work used a transient pulse heating technique to its advantage. In that way, the period of sample heating and cooling does not exceed several seconds under fairly adequate vacuum conditions, thus preventing sample oxidation.

Finally, this study is the second part of our previously initiated research on thermophysical properties of two transition metals at high temperatures. Paper describing the properties of hafnium has been already published in [10].

2. EXPERIMENT

As mentioned in the foregoing, two experimental methods were used: *subsecond pulse calorimetry* for measuring the specific heat capacity, specific electrical resistivity, hemispherical total emissivity, and normal spectral emissivity and the *laser flash method* for thermal diffusivity measurements. A general review of these techniques is given by Maglić et al. [11], while particular features for these methods are provided in Dobrosavljević and Maglić [12] and Milošević et al. [13].

2.1. Samples

In the subsecond pulse calorimetry one zirconium sample in the form of a thin rod, 211.80 ± 0.01 mm in length and 2.890 ± 0.009 mm in diameter, was used. In the laser flash measurements a thin disk, 3.078 ± 0.004 mm in thickness and 10.012 ± 0.002 mm in diameter, was used. The disk thickness and both sample diameters from one side and the wire length from another were measured with two calibrated micrometers with resolutions of 10 and 20 μm, respectively. Final dimensions and their expanded uncertainties (coverage factor of 2) were obtained statistically by repeated measurements. The densities of the rod (after the first heating) and the disk were 6482 ± 72 and $6495 \pm 42\,\mathrm{kg{\cdot}m^{-3}}$, respectively.

Both samples were annealed for 1 h at about 1140 K. The presence of impurities detected by subsequent chemical analysis is given in Table I. Analysis of gaseous elements was not performed.

According to Table I, the calculated density of the first sample is $6487\,\mathrm{kg{\cdot}m^{-3}}$, while that of the second one is $6493\,\mathrm{kg{\cdot}m^{-3}}$. Comparing these values with measured densities, one can conclude that potential gaseous elements were not present at a level of more than 10^{-2} mass%

Table I. Sample Impurities (in mass%)

Sample 1	Ca	Hf	Si	V	Fe	Mo	Ti
	0.095	0.05	0.03	0.017	0.008	< 0.005	0.002
Sample 2	Hf	V	Fe	Ti	Mn	Ca	Mg
	0.038	0.015	0.008	0.002	0.001	< 0.0003	< 0.0003

in both samples, neither before nor after the experiment. Therefore, the sample purity of Zr was, at least, 99.79 mass% for the rod and 99.94 mass% for the disk.

2.2. Measurements

2.2.1. Subsecond Pulse Calorimetry

The measurement technique, experimental procedure, and uncertainty assessment of the used method were described in our previous paper [10]. In this work, however, additional measurements of the sample surface radiation above 1000 K were carried out by using a calibrated high-speed pyrometer operating at $\lambda = 900\,\text{nm}$. The pyrometer was focused at the sample center, just above the thermocouple position and the normal spectral emissivity was determined from the difference between thermocouple and pyrometer signals.

All measurements (15 runs) were performed at a heating rate of $650\,\text{K}\cdot\text{s}^{-1}$. During a single run, the maximum temperature of the "effective" sample was from 1200 to 2100 K, while the initial temperature was always ambient. In order to minimize the influence of the Thomson effect, the direction of current was altered subsequently, run by run. During all experiments, undesired events, such as sample bending or some unusual temperature distribution along the sample, were not visually detected.

2.2.2. Laser Flash Method

Like those of the subsecond pulse calorimetry, the technique, experimental procedure, and uncertainty estimation of the used laser flash method were described in detail in [10].

A total of 86 measurements were carried out by using this technique. The sample temperature was changed from ambient temperature up to 1480 K, with an average step of 50 K, and three signals were recorded at each reference temperature. The sample was inspected between different series of experiments, and no physical changes of the sample were detected. Due to the laser beam interference with the colloidal carbon layer at the front side of the sample, the layer had to be renewed several times during the series of measurements.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Before performing data reduction and calculating thermophysical properties at various temperatures, it was necessary to apply corrections due to the effect of the sample linear thermal expansion. After the inspection of available data on the linear thermal expansion coefficient, α_T, literature values published by Petukhov [14] were taken as reference values to use in this work. He gave recommended values of this property for isotropic polycrystalline zirconium in the form of a polynomial:

$$\alpha_T = 5.7406 \times 10^{-6} + 1.1888 \times 10^{-9}(T - 293) + 7.0155 \times 10^{-13}(T - 293)^2$$

for the range between 293 and 1130 K and

$$\alpha_T = 1.8940 \times 10^{-6} + 3.9735 \times 10^{-9}(T - 293) + 1.0345 \times 10^{-13}(T - 293)^2 \quad (1)$$

for the range between 1200 and 1830 K. For the purpose of this work, the values of α_T were interpolated for temperatures between 1130 and 1200 K and extrapolated for those higher than 1830 K. The reported expanded uncertainty (coverage factor of 2) of recommended values of α_T is less than 3% [14], and this value was assumed in data reduction for the whole temperature range.

3.1. Hemispherical Total and Normal Spectral Emissivity

In order to compute the sample specific heat capacity from the subsecond pulse method, one needs to first estimate the temperature function of the hemispherical total emissivity, particularly at very high temperatures, where the influence of heat loss by radiation is significant.

The values of the hemispherical total emissivity were obtained from experimental data using different filtering and averaging algorithms. According to a procedure described in [12], measured values of the hemispherical total emissivity are rather discrete than continuous and, in addition, very sensitive to errors introduced from the fitting of derivative functions.

The raw results and a corresponding fitting function are presented in Fig. 1 and compared with available literature data. Values can be computed from the linear function:

$$\varepsilon_{\text{th}} = 0.1842027 + 7.142254 \times 10^{-5} T, \quad 1400\,\text{K} < T < 2000\,\text{K}. \quad (2)$$

with an expanded uncertainty (coverage factor of 2), $U_{\varepsilon\text{th}}$, of 3.0% and 2.5% for lower and higher temperature ranges, respectively. Since the influence of emissivity decreases at temperatures below 1400 K, the linear fit from Eq. (2) was used for heat capacity determination over the whole temperature range.

Comparisons with literature data show that the results from this study are consistent with those of Cezairliyan and Righini [15] and partially with

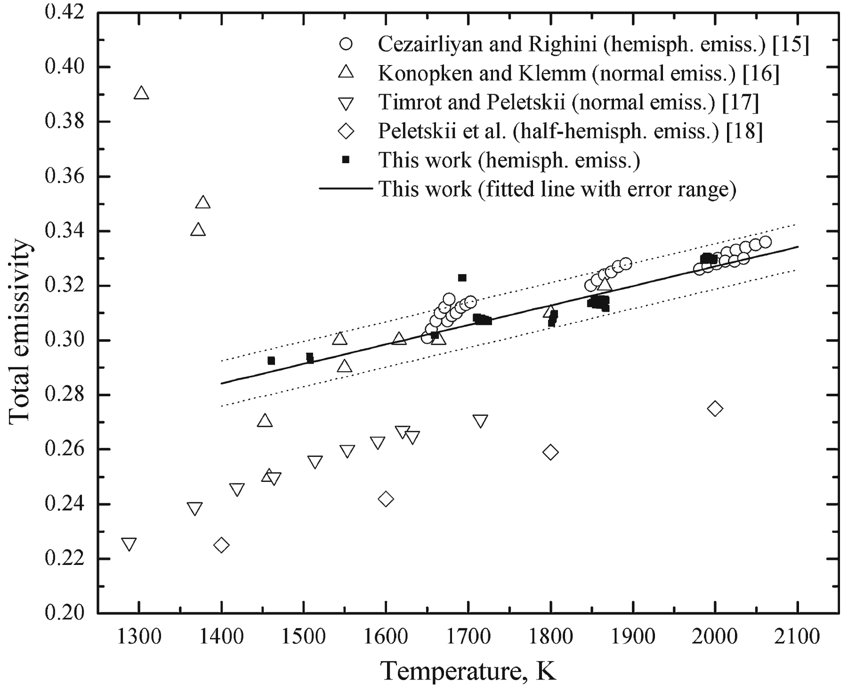

Fig. 1. Total emissivity of zirconium.

those by Konopken and Klemm [16] whose data, however, represent the *normal* total emissivity. The sample purity in [15] was 99.98%, while that in [16] was not reported. Present results are higher than those published by Timrot and Peletskii [17] and Peletskii et al. [18], but the former also measured the normal total emissivity, while the latter ones measured the half-hemispherical total emissivity of zirconium. The sample purity in [17] was at least 99.5%, while that in [18] was 99.9%.

Results from [16] cannot be discussed because the authors did not give more details about the sample and measurement method. On the other hand, differences between the present results and those from [17, 18] can be explained in the same manner as the authors of [15] have done, who also used the subsecond measurement technique. Repeated pulse heating and cooling over the transition temperature may change a polished and smooth surface to be uneven and rough. However, fast heating and cooling ensures minimal oxygen and nitrogen uptake by the zirconium sample, so the measured emissivity should correspond to a more pure specimen surface.

The problem of absorption was reported by Jain et al. [19], who, like the authors of [17, 18] also used a stationary state technique. Since their sample was oxidized already at 1300 K and even under a pressure of 0.1 mPa, Jain et al. [19] measured, in fact, the emissivity of zirconium oxide, instead of that of pure zirconium. The values of the total emissivity of such oxidized zirconium surface were in the 1050 to 1500 K range between about 0.46 and 0.50 and they are, as expected, much higher than those presented here. As a conclusion, therefore, the differences between the data from this work and those of [15] and the data from [17, 18] cannot be clearly explained with available information.

Regarding the normal spectral emissivity at 900 nm, final results and comparisons with some available literature data are given in Fig. 2. A general observation is that measured values of this parameter do not change much with temperature. They are comparable with data published by Coffman et al. [20] (representing extracted values at 900 nm from several measurements at different wavelengths), where one can notice a significant difference over the whole temperature range. Our data lie between those given for 2300 nm by Furman and McManus [21] and those for

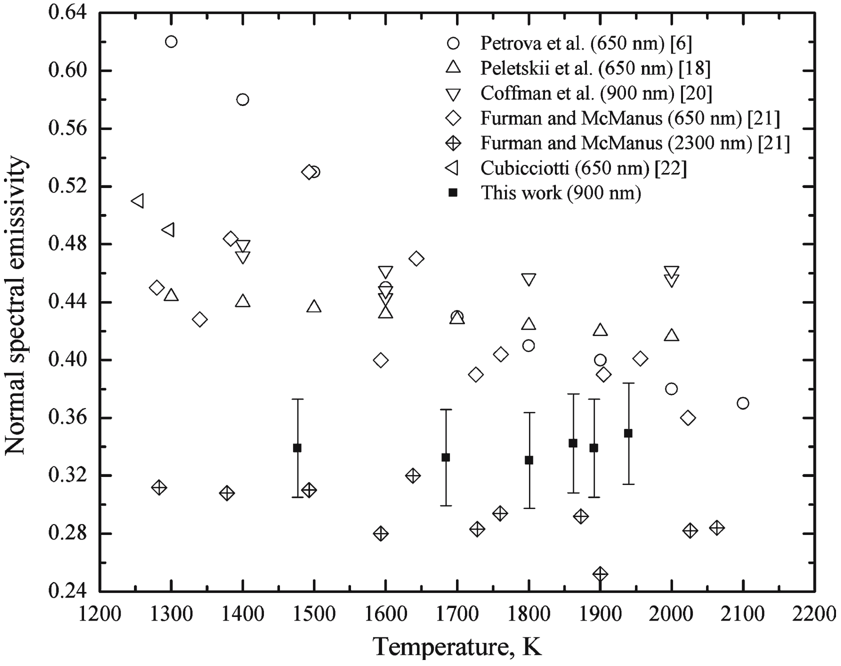

Fig. 2. Normal spectral emissivity of zirconium.

650 nm by the same authors [21], Cubicciotti [22], Peletskii et al. [18], and Petrova et al. [6].

The expanded uncertainty of the present results (coverage factor of 2) does not exceed 10%. The uncertainty of comparable values [20] was not reported.

3.1.1. Specific Heat Capacity

From experimental data for the voltage drop over the "effective" sample and the electric current during the heating, as well as thermophysical and other parameters of the sample, including that of the hemispherical total emissivity and specific heat capacity as a function of temperature was computed according to the procedure described in [12], without correction for impurities. The final results were obtained by averaging the data from all experiments. One averaging algorithm was applied in the range of the stable phase (hcp or bcc), and another in the range of the phase transition. The readout of final results at regular intervals, with the expanded uncertainty region (coverage factor of 2) marked with error bars, and the available literature data are shown in Fig. 3.

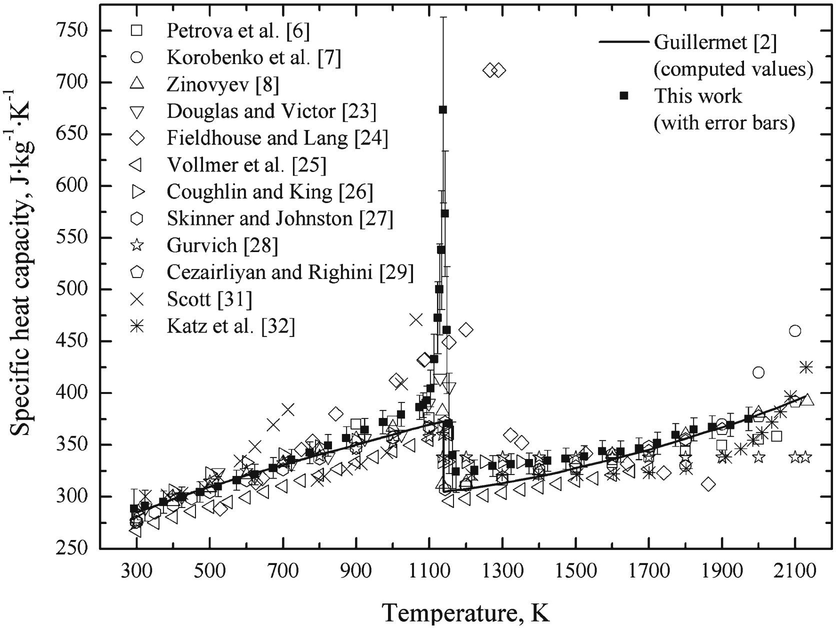

Fig. 3. Specific heat capacity of zirconium.

One important characteristic of the present data involves the heat capacity values inside the phase transition region. Namely, due to the transient nature of the temperature measurements, the heat capacity increases and falls rapidly as the temperature of the sample passes the phase transition region. Because of physical limitations found in rapid temperature measurements (finite characteristic response of the temperature detector and temperature gradient of the sample section different from zero), the phase transition in this method does not appear as a single point, such as may be observed by other techniques, but in some narrow temperature region. Except for Douglas and Victor [23] and Fieldhouse and Lang [24], no other authors cited in Fig. 3 reported the existence of such a region. For example, Vollmer et al. [25], who used an adiabatic calorimeter, measured the specific heat capacity up to 1070 K for the hcp phase and from 1200 K for the bcc phase, where, between these temperatures, they found a sudden change of heat capacity values. Nevertheless, they published an interpolated curve in that region, reporting a phase transition point of 1155 K as the temperature of the minimal gradient of the heat capacity change. On the other hand, Petrova et al. [6], who used subsecond calorimetry, clearly indicated an abrupt change of heat capacity, but did not evaluate its mean value.

In this work, the maximum value of the heat capacity of a single experiment in the region of the phase transition represents the inflection point (minimal gradient) at the sample transient temperature. The maximum averaged value of the heat capacity in this region (not shown in Fig. 3) was obtained at 1141.4 K, and that temperature, therefore, indicates an averaged phase transition point. The expanded uncertainty of this temperature (coverage factor of 2) is estimated to be about 10.5 K. Coughlin and King [26] reported a phase transition point of 1135 K, Skinner and Johnston [27] reported 1143 K, Douglas and Victor [23] and Gurvich [28] reported 1136 K, Vollmer et al. [25] reported 1155 K, and Cezairliyan and Righini [29], Zinovyev [8], and Petrova et al. [6] reported 1147 K. As a recommended value of this parameter, Touloukian and Buyco [30] gave 1135 K, while, as the most probable value of the hcp/bcc phase transition in zirconium, Guillermet [2] adopted 1139 ± 5 K.

In the hcp phase, most data found in the literature agree well with each other. Exceptions represent the early measurements of Scott [31] with a rather large scatter of results and the data of Fieldhouse and Lang [24]. Scott [31] used adiabatic calorimetry, and the scatter of his data might indicate the existence of chemical reactions in the sample. Although authors reported a high purity sample, the data of Fieldhouse and Lang [24] show a very wide approach to the peak, detecting the phase transition at a much higher temperature than other researchers, i.e., between 1250 and 1290 K.

Vollmer et al. [25] data with their almost linear rise up to the phase transition mark the lowest values. They used a sample with a purity of 99.8%; major impurities were oxygen and iron.

In the hcp phase, the present results are in good agreement with literature data, except in the temperature range approaching the phase transition region, where they are slightly higher than those of Coughlin and King [26], Skinner and Johnston [27], Gurvich [28], and those assessed by Guillermet [2]. However, the difference between the data of this work and, for example, those of Guillermet [2], does not exceed 6% at the very onset of the phase transition range (at about 1093 K).

In the bcc phase, our heat capacity values are again in general agreement with the bulk of literature data. The difference between them and the Guillermet recommended values [2] decreases as the sample temperature increases. In this phase, the values of Vollmer et al. [25] in the range from the phase transition to about 1600 K, where their measurements were performed, are the lowest. An interesting behavior of the heat capacity in this phase is shown by Gurvich [28], Katz et al. [32], and Korobenko et al. [7]. While the values from [28] are constant over the whole bcc phase range, those from [32, 7] show a significant rise with temperature from about 1800 K up to the melting point. Katz et al. [32] used levitation drop calorimetry with samples of 99.9% purity and with a reported error from 1.6% at lower temperatures to 12.2% at the melting point. Korobenko et al. [7] used a pulse heating technique with a very fast heating rate ($\sim 10^8\,\mathrm{K{\cdot}s^{-1}}$). The upswing of data at the highest temperatures might be attributed to the existence of point defects. Namely, according to Kraftmakher [33], the nonlinear rise of the specific heat capacity could be due to intensive vacancy formation at high temperatures. At these temperatures, point defects are particularly present in refractory metals, such as zirconium, tungsten, etc.

The values of our specific heat capacity results shown in Fig. 3 are presented in Table II, together with their expanded uncertainties (coverage factor of 2). It should be noted that these uncertainties were obtained by taking into consideration the errors of all parameters used in data reduction, such as sample dimensions, effective mass, and surface emissivity. At high temperatures, the contribution due to intensive radiation to the error of the hemispherical total emissivity is dominant. On the other hand, higher uncertainties at low temperatures and in the phase transition region were the consequence of wider data scatter in the corresponding temperature ranges.

Table II. Specific Heat Capacity of Zirconium and Maximum Estimated Uncertainties

T (K)	c_p (J·kg^{-1}·K^{-1})	U_{c_p}(%)	T (K)	c_p (J·kg^{-1}·K^{-1})	U_{c_p}(%)	T (K)	c_p (J·kg^{-1}·K^{-1})	U_{c_p}(%)
293	288.4	6.6	1073	386.2	3	1323	331.4	3
323	291.3	5.1	1083	388.3	3	1373	332.2	3
373	294.8	3.6	1093	392.9	3.5	1423	334.7	3
423	299.4	3.3	1103	404.3	4.3	1473	336.7	3
473	304.5	3.2	1113	432.8	5.6	1523	338.8	3
523	309.9	3.1	1123	472.7	7.4	1573	343.8	3
573	315.9	3.1	1128	500.1	8.8	1623	343.6	3
623	321.5	3.1	1133	538.1	10.7	1673	346.3	3
673	327.6	3.1	1138	673.3	13.3	1723	351.6	3
723	335.4	3.1	1143	573.2	10.6	1773	359.5	3
773	342.4	3	1148	460.8	13.3	1823	365.1	3
823	349.4	3	1153	370.8	13.1	1873	367.2	3
873	356.6	3	1163	339.8	9.5	1923	369.2	3
923	364.6	3	1173	324.3	6.2	1973	375.2	3
973	372	3	1223	325.7	3			
1023	379.3	3	1273	329.5	3			

3.2. Specific Electrical Resistivity

From the data of voltage drop and electrical current passed through the sample, the values of specific electrical resistivity were computed. Final results and available literature data are presented in Fig. 4. Values and their expanded uncertainties (coverage factor of 2) are given in Table III.

Compared with published data, our results coincide very well in both phases with those published by Cook et al. [34], Bostrom [35], Zinovyev [8], and Binkele and Brunen [4]. Cezairliyan and Righini [15] and Korobenko et al. [7] measured this parameter only at the highest temperatures, and the present results agree as well with their data. However, there are some more significant differences between these and some other data in the hcp phase. In this phase, authors of [3, 18, 36–41] obtained higher electrical resistivity results. Values from Saller and Dickerson [37], Rogers and Atkins [39], and Peletskii et al. [3, 18] differ significantly from other data, especially at the beginning of the phase transition point. While authors in [37] reported the use of a "sponge" zirconium sample, the others reported tests on relatively pure specimens. Regardless of this disagreement in the hcp phase, the differences decrease toward lower temperatures; so, at room temperature they are in close proximity to each other.

Interesting values of the specific electrical resistivity of zirconium were published by Mikryukov [40]. He used two samples: first, relatively pure (99.9%) and prepared by the iodide process and second, with at

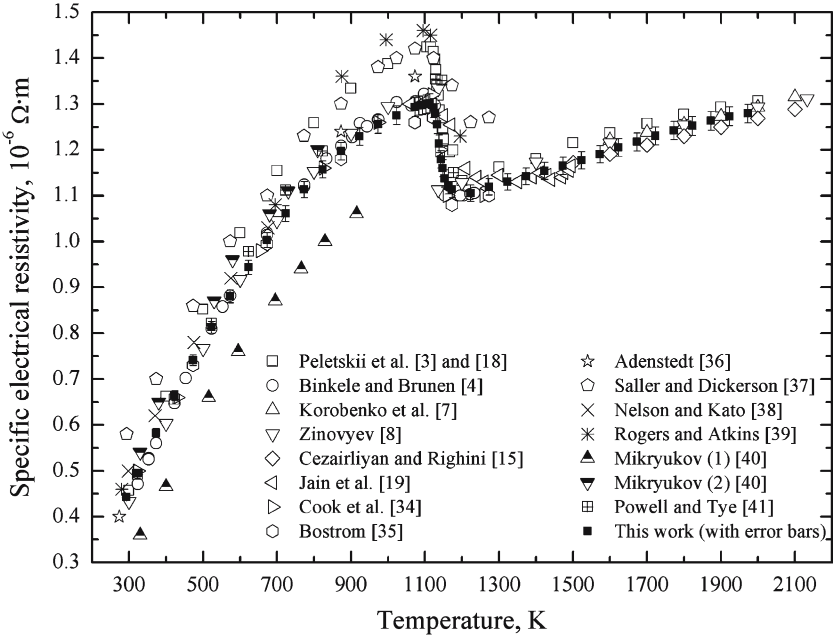

Fig. 4. Specific electrical resistivity of zirconium.

Table III. Specific Electrical Resistivity of Zirconium and Maximum Estimated Uncertainties

T (K)	$\rho(10^{-7}\Omega\cdot\mathrm{m})$	U_ρ (%)	T (K)	$\rho(10^{-7}\Omega\cdot\mathrm{m})$	U_ρ (%)	T (K)	$\rho(10^{-7}\Omega\cdot\mathrm{m})$	U_ρ (%)
293	4.43	1.6	1073	12.93	1.6	1323	11.3	1.6
323	4.95	1.6	1083	12.96	1.6	1373	11.42	1.6
373	5.83	1.6	1093	12.97	1.6	1423	11.54	1.6
423	6.64	1.6	1103	13	1.6	1473	11.65	1.6
473	7.41	1.6	1113	13.01	1.6	1523	11.77	1.6
523	8.13	1.6	1123	12.91	1.6	1573	11.9	1.6
573	8.8	1.6	1128	12.8	1.6	1623	12.05	1.6
623	9.44	1.6	1133	12.55	1.6	1673	12.17	1.6
673	10.03	1.6	1138	12.13	1.6	1723	12.3	1.6
723	10.61	1.6	1143	11.79	1.6	1773	12.42	1.6
773	11.13	1.6	1148	11.6	1.6	1823	12.52	1.6
823	11.57	1.6	1153	11.37	1.6	1873	12.63	1.6
873	11.97	1.6	1163	11.21	1.6	1923	12.73	1.6
923	12.29	1.6	1173	11.13	1.6	1973	12.79	1.6
973	12.56	1.6	1223	11.05	1.6			
1023	12.75	1.6	1273	11.19	1.6			

least 0.22% impurities (mostly Hf and C). Data from the second sample coincide generally with other literature values, while those from the first sample are significantly lower.

In the phase transition region, Jain et al. [19] reported a smooth descent of specific electrical values. Outside that region, however, their values agree well with others, in spite of detected oxidation of the sample.

The expanded uncertainty of the present results was practically constant, 1.6% over the whole measured temperature range. In addition to the regular changes of sample dimensions because of the linear thermal expansion, the influence of sample elongation due to repeated heating and cooling was also accounted for in the calculation of measurement error.

3.3. Thermal Diffusivity

The thermal diffusivity was measured by using the laser flash method and the second sample from Table I. According to the applied data reduction procedure, the results for each narrow temperature region were averaged. Final results are presented in Fig. 5, together with available literature data. Corresponding values and their expanded uncertainties (coverage factor of 2) are given in Table IV.

Only a few sets of literature or reference data have been found. Touloukian et al. [9] gave recommended values of the thermal diffusivity for a polycrystalline sample with an uncertainty level of 10% in the region from room temperature up to 800 K and provisional values above 1000 K with a 20–25% uncertainty level. McIntosh et al. [42] reported data for an isotropic sample with less than 0.5% impurities and an error of 5%. They used a periodic measurement technique based on one-dimensional heat flow only up to about 400 K. Pollard [43] applied a modified Angström method on a cylindrical zirconium sample, also with less than 0.5% impurities, but reported no information on measurement error. He measured the thermal diffusivity from room temperature up to the phase transition. The laser flash method was used both by Murabayashi et al. [44] and Takahashi et al. [45]. Both groups reported testing of high-purity samples, but did not report data on the analysis of the samples. For both groups, measurements at temperatures below the phase transition were performed. The reported errors were 1.5% in [44] and less than 5% in [45]. Finally, Zinovyev [8] proposed reference data on the thermal diffusivity of zirconium over a wide temperature range, covering both hcp and bcc phases. In that study, however, no information on measurement uncertainties was reported.

The values from this work coincide well with those from Takahashi et al. [45] in the region from 300 to 500 K and with those from Touloukian et al. [9] from 750 K up to the beginning of the phase

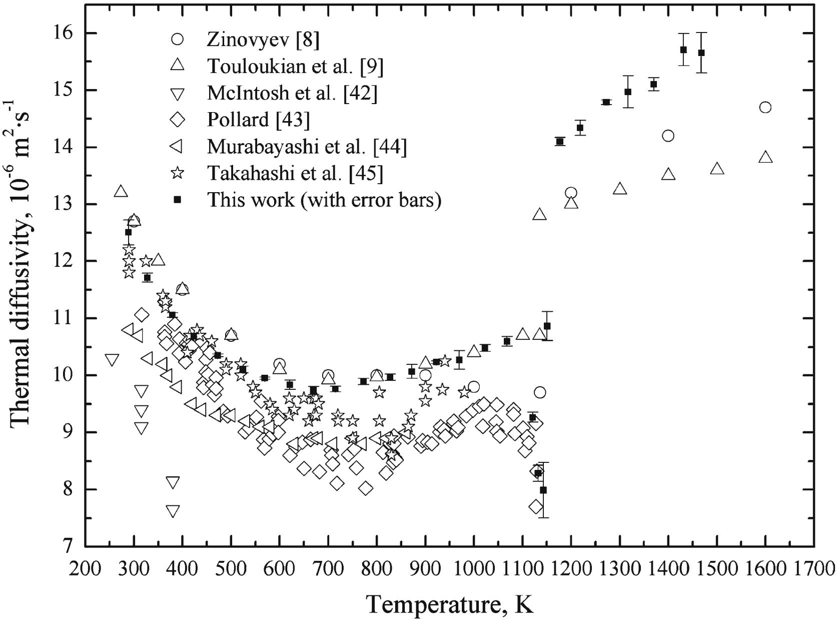

Fig. 5. Thermal diffusivity of zirconium.

Table IV. Thermal Diffusivity of Zirconium and Maximum Estimated Uncertainties

T (K)	$a(10^{-6}\,\mathrm{m^2{\cdot}s^{-1}})$	U_a (%)	T (K)	$a(10^{-6}\,\mathrm{m^2{\cdot}s^{-1}})$	U_a (%)
289	12.5	1.7	970	10.27	1.6
327	11.71	0.7	1023	10.48	0.6
379	11.06	0.4	1068	10.6	0.8
423	10.68	0.5	1121	9.27	0.9
473	10.35	0.2	1132	8.29	1.7
524	10.11	0.6	1143	7.99	6
569	9.95	0.2	1150	10.87	2.3
621	9.84	0.8	1177	14.1	0.5
670	9.74	0.7	1218	14.34	0.9
715	9.76	0.5	1272	14.79	0.3
772	9.89	0.6	1317	14.97	1.9
827	9.97	0.5	1370	15.1	0.8
872	10.07	1.2	1431	15.71	1.8
923	10.23	0.2	1468	15.66	2.3

transition region (approximately 1070 K). At high temperatures, in the bcc phase, our results are the highest, far above those predicted by Touloukian et al. [9] and measured by Zinovyev [8]. However, if one considers recommended uncertainties for this temperature range from 9, the data from this work are in general agreement with the present results.

According to our study and that from Pollard [43], there is a sudden drop of thermal diffusivity values over a short temperature range of the hcp/bcc phase transition. Moreover, our data and those from [43] are in an excellent agreement. Zinovyev [8] also reported a decrease of thermal diffusivity values as the sample temperature approached the phase transition, but his values differed from the other two.

As the measurement of the thermal diffusivity by the laser flash method is discrete in the sense of the sample reference temperature, the phase transition point cannot be precisely determined by this technique. However, according to the general behavior of measured thermal diffusivity values from this study (Fig. 5 and Table IV), the temperature of the phase transition of the zirconium sample used in this study could be estimated to be about 1143 ± 3 K. Such a temperature coincides well with that estimated in Section 3.2. This result served as a good foundation for subsequent thermal conductivity evaluations.

3.4. Thermal Conductivity and Lorentz Number

Having the measured values of specific heat capacity, specific electrical resistivity, and thermal diffusivity and computing the values of density with the use of data on linear thermal expansion adopted from [14] (Eq. (1)), the thermal conductivity and Lorentz number of zirconium were evaluated as a function of temperature. For the evaluation of thermal conductivity, one needs to use a unique value of the sample density as a function of temperature, so an average value of $6488 \pm 42\,\mathrm{kg \cdot m^{-3}}$ was taken.

Computed values of the thermal conductivity with uncertainty limits and selected literature data are presented in Fig. 6. It can be seen that thermal conductivity values for the present work do not vary as much as those of the heat capacity and thermal diffusivity in the region of the phase transition. The existence of some sudden variation of thermal conductivity in that region is visible, but it is, in fact, accompanied by higher uncertainty values, as expected.

In addition to the results from this study, some selected literature data on the thermal conductivity of zirconium are also presented in Fig. 6. Touloukian et al. [46] gave recommended values for polycrystalline zirconium based on previous experimental data. The uncertainty of those values was assessed as 5% at room temperature, increasing to 15% at higher temperatures. Recently, Fink and Leibowitz [5] published a recommended function for the thermal conductivity of zirconium from 300 to 2000 K, which was the result of a detailed analysis of numerous previous literature

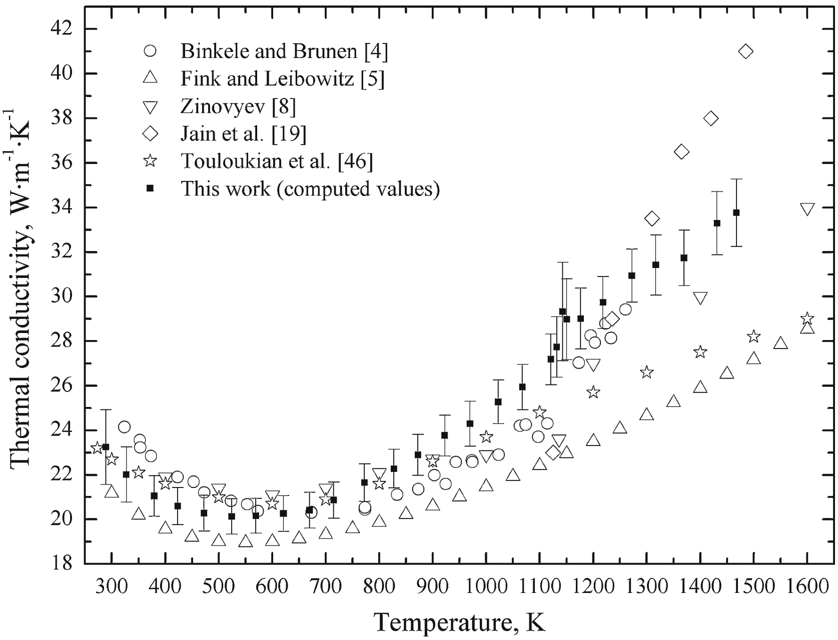

Fig. 6. Thermal conductivity of zirconium.

data. The error limits of their recommended values vary from 5% to 9.5%, depending on temperature. Finally, three studies that were not covered by the analysis in [5] are also presented in Fig. 6: these of Jain et al. [19], Zinovyev [8], and Binkele and Brunen [4].

Jain et al. [19] measured the thermal conductivity only above 1100 K and gave no information about sample purity. Their values increase with temperature almost linearly. According to all other published data, the thermal conductivity of zirconium virtually follows a parabolic function in the temperature range of consideration. Up to about 1000 K, the present data coincide well with those proposed by Touloukian et al. [46], while above that temperature they are generally higher than other data, except for those by Jain et al. [19]. However, taking in consideration the uncertainty limits of recommended values and the possible errors of other reference data at high temperatures, the agreement between our results and other data is better in that temperature region.

At temperatures above 1300 K, a slight decrease in the slope of the thermal conductivity versus temperature curve was detected in this research. A similar behavior, but with lower mean values, was suggested by Touloukian et al. [46].

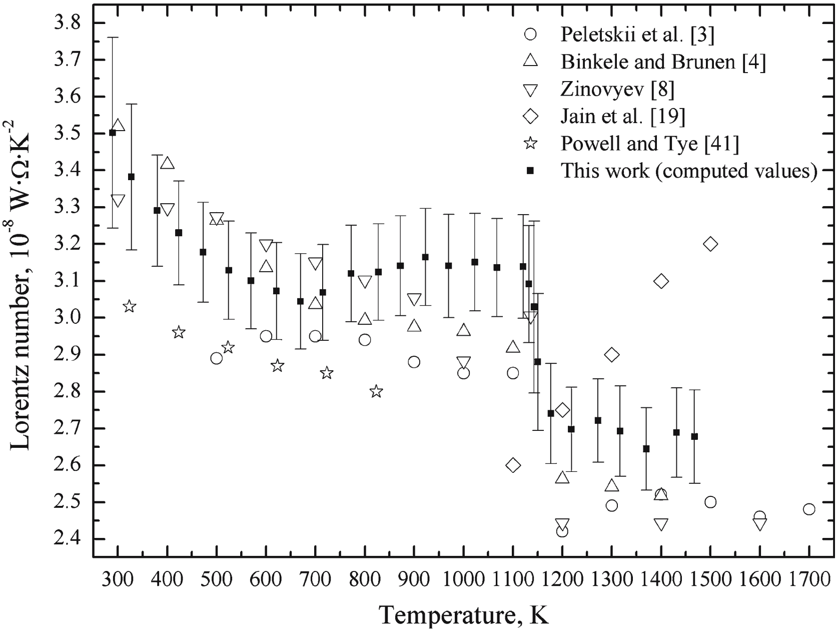

Fig. 7. Lorentz number for zirconium.

Regarding the Lorentz number, computed values of this parameter are shown in Fig. 7, together with previously published data. Variation of our results depends on the temperature range. After a relatively rapid decrease from ambient temperature to about 650 K, the Lorentz number is relatively constant until the phase transition region. After the phase transition, in the sample bcc phase, the Lorentz number falls to a value of about 2.7×10^{-8} W·Ω·K^{-2}, without any indication of further significant variation. These results are in good agreement with those of Binkele and Brunen [4] over the whole temperature range, and, partially, with the values of Zinovyev [8] in the hcp phase. The latter author reported no difference between the Lorentz number (2.443×10^{-8} W·Ω·K^{-2}) in the hcp phase and that in the sample bcc phase.

Although the concentration of sample impurities was not high in the present work (see Table I), these results on the Lorentz number indicate the presence of electronic scattering due to the imperfections of the sample structure.

All computed values of thermal conductivity and Lorentz number, together with their expanded uncertainties (coverage factor of 2), are given in Table V.

Table V. Thermal Conductivity and Lorentz Number of Zirconium with Maximum Estimated Uncertainties

T (K)	λ ($W\cdot m^{-1}\cdot K^{-1}$)	U_λ (%)	L ($10^{-8} m^2\cdot s^{-1}$)	U_L (%)	T (K)	λ ($W\cdot m^{-1}\cdot K^{-1}$)	U_λ (%)	L ($10^{-8} m^2\cdot s^{-1}$)	U_L (%)
289	23.24	7.2	3.502	7.4	970	24.29	4.2	3.14	4.5
327	22.01	5.6	3.382	5.9	1023	25.27	3.9	3.151	4.2
379	21.05	4.3	3.291	4.6	1068	25.94	3.9	3.136	4.2
423	20.6	4.1	3.23	4.4	1121	27.18	4.2	3.139	4.5
473	20.28	3.9	3.178	4.3	1132	27.74	4.9	3.092	5.1
524	20.14	3.9	3.129	4.3	1143	29.33	7.5	3.029	7.7
569	20.16	3.9	3.1	4.2	1150	28.98	6.2	2.88	6.4
621	20.27	4	3.072	4.3	1177	29.01	4.7	2.74	5
670	20.41	3.9	3.045	4.2	1218	29.73	3.9	2.697	4.3
715	20.87	3.9	3.069	4.2	1272	30.93	3.8	2.721	4.2
772	21.65	3.9	3.12	4.2	1317	31.42	4.3	2.693	4.6
827	22.28	3.9	3.124	4.2	1370	31.74	3.9	2.644	4.2
872	22.9	4	3.141	4.3	1431	33.29	4.2	2.689	4.5
923	23.77	3.8	3.165	4.2	1468	33.76	4.5	2.677	4.7

4. CONCLUSION

Although many reference data on the thermophysical properties of solid zirconium exist in the literature, there is still a need for further experimental investigations. Namely, the data on some properties are scarce and/or too much dispersed. For example, only one experimental data point was found on the thermal diffusivity of zirconium in the bcc phase. Also, many differences were found among the published data for the specific electrical resistivity.

The results of this research showed good agreement with data from many previous studies, especially with those measured using the same experimental techniques. Moreover, taking into consideration the reported and possible uncertainties of literature data, the present results confirm some previously reported regularities in the behavior of the thermophysical properties of zirconium versus temperature.

This study also offers some new and unexpected information. The reported thermal diffusivity is higher than other reference values in the sample bcc phase, and there is a significant and sudden variation of this property in the region of the phase transition. Consequently, the thermal conductivity in that region is also higher than most other literature data, but not the highest. However, independent of the large and opposite variation of the specific heat capacity and thermal diffusivity in the phase transition region, the computed thermal conductivity slope is rather smooth as opposed to irregular, confirming expectations. Finally, there is a significant difference between the present and corresponding literature values of the normal spectral emissivity measured at 900 nm, which calls for further research.

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